PREPARATION AND CHARACTERIZATION OF KENAF FILLED NATURAL RUBBER LATEX FOAM

by

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LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
DRC	Dry Rubber Content
FTIR	Fourier Transform Infrared Spectrometry
ISO	International Standards Organization
KOL	Potassium oleate soap
LA-TZ	Low ammonia TMTD and ZnO preserved
MST	Mechanical stability time
NR	Natural Rubber
NRL	Natural Rubber Latex
NRLF	Natural Rubber Latex Foam
PUF	Polyurethane foam
SEM	Scanning Electron Microscopy
SSF	Sodium silica fluoride
TGA	Thermogravimetric Analysis
TSC	Total solid content
VFA	Volatile fatty acids content
ZDEC	zinc diethyldithiocarbamate
ZMBT	zinc 2-mercaptobenzhiozolate
phr	Part per hundred of rubber
DPG	Diphenyl guanidine

LIST OF SYMBOLS

ρ	Density (Kg/ m^3)
^oC	Degree Celsius
V	Volume
M	Molar mass
MW	Molecular weight
MPa	Mega Pascal (10^6 Pascal)
^oC/min	Degree Celsius per minute
Kg	Kilo gram
Qf	Interaction Index of Filled Rubber
Qg	Interaction Index of Gum Vulcanizate
Qf/Qg	Rubber-Filler Interaction Index
T	Temperature
wt %	Weight percent

PENYEDIAAN DAN PENCIRIAN BUSA LATEKS GETAH ASLI TERISI KENAF

ABSTRAK

Kenaf telah menarik minat yang mendalam sebagai bahan pengisi dalam komposit matriks polimer (PMC) kerana kosnya yang rendah, jumlahnya yang banyak, dan keupayaannya untuk meningkatkan sifat-sifat seperti kekuatan tegangan dan modulus, rintangan kimia dan kestabilan terma di dalam PMC. Walau bagaimanapun, penyerakan yang lemah serta ketidakserasian kenaf di dalam NRLF masih kekal sebagai isu yang mencabar bagi aplikasi praktikal dalam pelbagai persekitaran. Dalam kajian ini NRLF terisi kenaf yang mengandungi 0 hingga 7 bahagian seratus getah (phr) telah disediakan melalui kaedah pemprosesan Dunlop. NRLF terisi kenaf memperlihatkan pengurangan kekuatan tegangan, rintangan pembengkakan dan sifat kestabilan haba NRLF terisi kenaf berbanding dengan NRLF yang tidak terisi. Interaksi fizikal melalui penembusan dan / atau saling hubungan rantai NRLF di permukaan kenaf yang lemah menyumbang kepada rekatan antaramuka yang lemah di antara kenaf dengan NRLF yang mengakibatkan penurunan sifat-sifat NRLF terisi kenaf. Walau bagaimanapun, dengan beberapa pengubahsuaian kepada kenaf dan NRLF, sifat-sifat NRLF terisi kenaf telah meningkat. Kajian mengenai penggantian separa kenaf oleh kanji jagung dijalankan untuk menentukan potensi kanji jagung sebagai gantian untuk kenaf dalam komposit NRLF. Lima jenis komposit NRLF terisi kenaf / kanji dengan pembebanan pecahan kenaf / kanji yang berbeza (iaitu 7/0, 5/2, 3.5 / 3.5, 2/5 dan 0/7 phr) telah disediakan. Penggantian separa kenaf oleh kanji jagung sebagai pengisi bersama menghasilkan komposit pengisi hybrid yang menunjukkan potensi besar sebagai pengisi bersama dengan komposit kenaf NRLF, di mana sifat tegangan, rintangan pembengkakan, mampatan dan kekerasan

semakin meningkat dengan peningkatan dalam pecahan pembebanan pengisi kanji jagung. Kestabilan haba pula adalah lebih tinggi pada pecahan 3.5 / 3.5 kenaf/kanji. Berdasarkan siri kajian ini, kanji jagung kemudiannya digunakan sebagai pengisi bersama dalam NRLF terisi kenaf dengan menghadkan pembebanan kanji (3 phr). Keputusan menunjukkan bahawa kekuatan tegangan, pemanjangan pada putus, rintangan pembengkakan, kekerasan, kestabilan haba lebih tinggi berbanding dengan sampel tanpa pengisi jagung. Kajian morfologi oleh SEM menunjukkan bahawa sampel yang mengandungi pengisi jagung mempunyai saiz liang yang lebih kecil dan taburan liang yang lebih baik. Kesan kenaf yang dirawat dengan rawatan alkali pada sifat-sifat NRLF terisi kenaf kemudian dikaji secara berasingan. Penyebaran kenaf dalam NRLF dan rekatan antaramuka di antara kenaf dan NRLF dipertingkatkan dengan penambahan kenaf yang dirawat telah menyumbang kepada peningkatan sifat-sifat tegangan, kekerasan, mampatan, kestabilan termal dan rintangan pembekakan NRLF terisi kenaf. Penggunaan *prevulcanized* NRL telah menunjukkan peningkatan beberapa sifat NRLF terisi kenaf. Keputusan menunjukkan bahawa masa yang optimum untuk *prevulcanized* NRL adalah 24 jam. Dengan membandingkan antara sampel tanpa prevulcanized dan, sampel dengan prevulcanized, sampel *prevulcanized* NRLF menunjukkan ciri-ciri tegangan, rintangan pembengkakan, ketumpatan, kekerasan dan kestabilan haba yang lebih baik disebabkan oleh kesan ketumpatan sambung silang. Kajian morfologi menggunakan SEM menunjukkan rekatan antara muka yang baik dan keseragaman liang untuk *prevulcanized* NRLF terisi kenaf.

PREPARATION AND CHARACTERIZATION OF KENAF FILLED NATURAL RUBBER LATEX FOAM

ABSTRACT

Kenaf fiber have attracted great interest as filler material in polymer matrix composites (PMC) due to its low cost, and the ability to enhance properties such as tensile strength and modulus, chemical resistance and thermal stability of PMC. However, poor dispersion and incompatibility of kenaf in NRLF still remain as challenging issue for their practical application in various environment. In this research kenaf filled NRLF composite containing 0 to 7 part per hundred rubbers (phr) of kenaf loading was prepared through a well-known Dunlop processing method. Kenaf filled NRLF shows reduction of tensile properties, swelling resistance and thermal stability properties of kenaf filled NRLF composites as compared to the unfilled NRLF. The less physical interaction via penetration and/or interlocking of NRLF chains at kenaf surface contributed to weak interfacial adhesion between kenaf and NRLF which leads to the decreased in properties of kenaf filled NRLF composites. However, with some modification to the kenaf and NRLF, the properties of kenaf filled NRLF were improved. Studies on the partial replacement of kenaf by starch were carried out to determine the potential of starch as replacement for kenaf in NRLF composites. Series of five composites of kenaf/starch filled NRLF composites with different kenaf/starch fraction loading (i.e. 7/0, 5/2, 3.5/3.5, 2/5 and 0/7 phr) were prepared. Partial replacement of kenaf by starch produced hybrid filler composites showed great potential as co-filler with kenaf NRLF composites, at which the tensile properties, swelling resistance, compression and hardness was improved with increased in starch fraction. The thermal stability was higher at 3.5/3.5 kenaf/starch

fraction. Based on this series of studies, the corn starch was then used as a co-filler in the formulation of kenaf filled NRLF with fix amount of starch (3 phr). The results show that the tensile strength, elongation at break, swelling resistance, hardness, thermal stability and density were higher compared with samples without corn starch. The morphological study by SEM shows that samples with co-filler have smaller pores size and better distribution. The effect of treated kenaf by alkaline treatment on the properties of kenaf filled NRLF composites were then studied separately. The dispersion of kenaf in NRLF and interfacial adhesion between kenaf and NRLF was further enhanced with the addition of treated kenaf, which enhanced tensile properties, hardness, compression, thermal stability and swelling resistance of the kenaf filled NRLF composites. The used of prevulcanized NRL shows the improvement of several properties of kenaf filled NRLF. The results show that 24 hours was the optimum time for prevulcanization of NRL. By comparing with samples without prevulcanized, samples with prevulcanized NRLF shows higher tensile properties, swelling resistance, density, hardness and thermal stability due to the crosslink density effects. Morphological study by using SEM shows the good interfacial adhesion and uniform pores size of kenaf filled prevulcanized NRLF.

CHAPTER ONE

INTRODUCTION

1.1 Overview

Natural rubber (NR) is one of the cell components of numerous plant species (Annamma et al., 1990; Ciesielski 1999). Only 2000 from the several thousands of lactiferous species in the forest contain rubber in their latex and roughly 500 of them contain too little rubber to be considered as a potential source of NR (Cornish et al., 1993). From thousands of lactiferous species, Hevea brasiliensis, is presently the most important source of NR and the other rubber bearing plants are of minor importance. Havea brasiliensis is a forest tree that is indigenous to the tropical rain forests of Central and South America. (Blackey, 1997; George and Panikkar, 2000).

Over the past few years, most of the rubber for the world industry came from wild Hevea brasiliensis, Ficus elastica and Castilla elastica trees (Perumal et al., 2013). These trees growing in the forests of Central and South America, India and Africa. South and Central America were the main providers to rubber production with a 71% share in 1876. Due to rapid economic growth and demand throughout the world, rubber manufacturing in Europe and America had to broaden the source of supply of their raw material. Rubber agriculture in South East Asia was thus initiated in order to feed the industries located in Europe. In 1876, Henry A. Wickham collected 70,000 Hevea seeds from Brazil and brought them to the London's Royal Botanic Garden, of which only 2,700 seemed to have germinated, and 1,919 seedlings were sent to Ceylon. During the early days of rubber,

Ceylon became the center of activity for rubber seeds and seedlings supply. The growth of plantations in South East Asia was favored by rapid developments in the transportation sector and the opening of the Suez Canal. By the end of the 19th century, NR became one of the major plantation crops under colonial patronage with an export-oriented estate system of production. South East Asia has remained the predominant natural rubber producing region since then (Subramaniam, 1987; Thomas and Panikkar, 2000).

Malaysia was the top five of NR latex production in the world. NR latex was obtained from the tapping process of Hevea Brasilienisis plantation and it was use for production of different type of rubbery goods. Figure 1.1 shown the Malaysia's NR consumption from year 2000 until March of 2016. Based on Figure 1.1, the total NR consumption shown an increment of 30 % from year 2000 to year 2015 in Malaysia (Malaysia Rubber Board, 2016). The growing of NR consumption explained that NR was still an important raw material for the production of gloves in Malaysia.

NR latex was a preferred raw material for latex end products manufacturers around the world due to ease of processing and the excellent performance of latex end products in critical environments. The major production of latex products were gloves, condoms, catheters, foams and latex thread. The natural rubber latex foam industry saw the beginning of its true development in the late 1920's was no accident but in many ways a fulfillment. There are two process for NRLF which is Talalayt process and Dunlop process. Development of the Dunlop process have formed the basis of what became one time the most important process for the manufacture of latex rubber (Blackley, 1966). The Dunlop process is particularly well adapted to the manufacture of molded latex foam products of thick section such as pillows, cushions, mattresses and upholstery foam

(Roslim et al., 2012). Morosely, very few research works have been done on natural rubber latex foam.

However to best of our knowledge, there are no published reports on attempts to incorporate kenaf powder into natural rubber latex foam. Therefore this study is focused on the development of environmental friendly kenaf filled natural rubber latex foam.

1.2 Brief introduction of natural rubber latex foam

In early 1914, Schidrowitz and Goldsbrough make an attempt to produce a porous rubber product from NRL concentrates, called "latex foam" (Ramasamy et al. 2013). Latex foam can be defined as a cellular rubber that has been made directly from liquid latex. One of the well-known processes to make latex foam was called Dunlop process which mainly used in manufacturing of thick molded latex foam products such as pillows, cushions and mattresses (Ramasamy et al. 2013).

In the process of making NRLF from NRL, a stable dispersion of NRL and chemicals are being converted to a stable porous solid material. In this conversion several important steps should be followed such as making of air bubbles inside the liquid dispersion system, stabilizing the air bubbles in the dispersion, solidifying/gelling of the liquid dispersion phase without disturbing the air bubbles, vulcanizing of rubber particles of the dispersion phase and finally removing the remaining liquid phase while making a stable solid-gas system known as cellular/sponge material (Calvert et al., 1982).

The most common used of foam nowadays were polyurethane foam (PU foam) which is synthesized using chemicals and natural rubber latex foam (NRLF) derived from

natural rubber latex. Natural rubber latex foam is widely used in bedding and furniture industries for manufacturing mattresses, pillows, sofa cushions, and in automobile products such as car seats, cushions, insulation materials (Madge, 1962). Enormous amount of foam materials are used in various environment and conditions which required scientist to developed a foams based on required needs.

1.3 Problem statement

Nowadays, the commercial foam usually comes from the petroleum oil based product like polyurethane (PU) foam, polyethylene (PE) foam, polystyrene (PS) foam and polycarbonate (PC) foam. Petroleum is a non-renewable resource that need to be conserved as it faces a serious depletion problem. Petroleum oil based product need longer time to decompose in our environment. Thus, they can exist as a large number of solid waste and causing land pollution. Furthermore, burning thermoplastic foam especially the PU foam could also harm to our environment. Burning the PU foam can produce a large amount of toxic gases which affecting the society. It can produce hydrogen cyanide (HCN) and carbon monoxide (CO) gases which can leads to lung damage and causing death (Mckenna and Hull, 2016). There was a report stated that a number of 35 convicts in a prison died in a burning of PU foam in 1990 (Liu and Gaan, 2016) synthetic or blended latex. The NRLF has been used in the bedding and furniture industries for manufacturing mattresses, pillows and automobile products like car seats, cushions and insulation materials (Ramasamy et al., 2012). However, the NRLF is quite expensive in comparison to the synthetic foam due to their natural properties which is incredibly

resilient. Addition of fillers will reduce the cost of latex production with comparable properties (Ramli and Hashim, 2010).

The utilization of natural fibers have been widely used in many application like construction, biomedical, aircraft spare parts and military vehicles due to their superior properties (Ishak et al., 2010; Namvar et al., 2014). The types of natural fibers that are commonly used in polymeric material includes kenaf, abaca, bamboo, hemp, flax, sisal and grass (Yıldızhan et al., 2018). Natural fibers offer an environmental advantage, with specific strength and low cost, thus making the products become more attractive (Joshi et al., 2004).

Many researches have been carried out to utilize natural fibers as filler in the polymer material either in rubber (El-Sabbagh et al., 2001; John et al., 2008; Som and Mustafa, 2010; Ismail et al., 2012; Shahril et al., 2017) or thermoplastic (Chow et al., 1998; Ribot et al., 2011; Pang and Ismail, 2014). Natural fibers have become the preference over the synthetic fibers due to their cost effectiveness, can be derived from renewable resources and have competitive specific mechanical properties (Izran et al., 2014). The incorporation of fibers into NRLF also has been reported by Ramasamy et al. (2012). Thus, this study is focusing on the development of green foam in order to minimize the environmental problems.

In this research, combination of kenaf with natural rubber latex to make an environmental friendly natural rubber latex foam products would lead to a stunning polymeric sponge material for a various foam application such as mattresses, pillow, sound absorbance, oil absorbance, packaging and etc. As explained above, foam materials

having kenaf as a biofillers can lead to a totally green composites which helps to reduce environmental problems.

1.4 Objective of study

The main objective of this research work was to prepared and characterized kenaf filled NRLF. The main objective can be divided into few sub-objectives which are as follows:

I. To characterize kenaf and investigate the effect of kenaf loading on the tensile properties, swelling, rubber filler interaction, density, compression, hardness, thermal stability and morphological properties.

II. To study and compare the effect of partial replacement of kenaf by corn starch as a co-filler on the properties of kenaf filled NRLF.

III. To study and compare the effect of corn starch as a co-filler on the properties of kenaf filled NRLF.

IV. To study and compare the effect of treated kenaf by alkaline treatment on properties of kenaf filled NRLF.

V. To study and compare the effect of maturation time of NRL on the properties of kenaf filled NRLF.

1.5 Important and contribution of study

By adding kenaf fiber (natural filler) into the Natural Rubber Latex Foam NRLF, the overall production cost of NRLF can be reduced for suitable applications. The non-

degradation of NRLF can be reduced due to the biodegradable properties of kenaf hence give the positive impact to the environment. Furthermore, kenaf started to commercialize in Malaysia when the demand of the timber was increased and at the same time the rate of deforestation also increased. The deforestation caused several adverse effects to the biodiversity of agricultural land. Kenaf has been a great choice to encounter deforestation issues as kenaf is a non-wood crop that produced paper and other products without causes any harmful to the environment. Thus, the usage of kenaf fiber can improve the sustainability effect on the environment. Among the benefits that could be obtained from this research work is as follows:

I. Research have been intended as an effort to utilize kenaf fiber obtained from Kenaf and Tobacco Malaysia as a potential filler in NRLF which not only reduces the production cost of NRLF based composites but also contributes to the economic growth.

II. Innovation to introduce kenaf as a filler in NRLF composites which is non-hazardous and pollution free, as well as to retain the properties of NRLF composites to meet the product specifications.

III. Preparation of kenaf filled NRLF composites with uniform pores can enhanced tensile properties, thermal stability, swelling resistance and mechanical properties through the simplest and affordable, latex compounding method using mixer.

1.6 Scope of study

Based on the objectives of this research, the reinforcing ability of kenaf in NRLF was evaluated by narrowing down the scope of study to investigate the tensile properties, swelling resistance, rubber filler interaction, hardness and compression and thermal stability. Meanwhile the morphological analysis using scanning electron microscope (SEM) and Fourier Transform Infra-Red (FTIR) analysis were conducted for further evaluation and as to support any improvements in the properties of kenaf filled NRLF.

This research is divided into five main stages which can be described as follows:

I. The characterizations of kenaf and NRL which includes FTIR, SEM analysis and basic latex testing analysis to identify the functional groups and chemical elemental compositions of kenaf latex respectively, and the morphological study to observe the shape and surface morphology of kenaf particles. This stage is important to compare and confirm that kenaf have the typical features as that of the commercially available fillers materials.

II. Preparations of kenaf filled NRLF as function of kenaf loading and to several properties of the composite. The possible reinforcement mechanism of kenaf in NRLF was suggested with proper evidence to prove that kenaf can be used as filler in NRLF.

III. The comparison of partial replacement of kenaf by corn starch as a co-filler in NRLF and deciding whether starch can be used either to replace or used as a co-fillers with kenaf in NRLF.

IV. Improvisation of the properties of kenaf filled NRLF composite with the addition of corn starch as a co-filler. This stage also includes the preparations and

characterization of kenaf filled NRLF with the effects of co-filler by using a Dunlop methods. All the possible reinforcement mechanism imparted between kenaf and NRLF were suggested and confirmed with proper evidence.

V. Kenaf was treated by using alkaline treatment and the effects of treated kenaf on NRLF were characterized. The mechanism of kenaf and NRLF was suggested with proper evidence to prove that treated kenaf can enhance the properties of NRLF.

1.7 Thesis organization

This thesis was divided into 5 chapters, which each covers the research interest based on the objectives of this research.

1. **Chapter 1:** Chapter 1 contains the introduction to the thesis. It includes the general introduction and overview of the research background, the problem statements, the importance of this research work, objectives of the project, the scope of study and the thesis organization.
2. **Chapter 2:** Chapter 2 contains the reviews of previous research findings related to current research work reported in this thesis. It also contains some general overview on NRL, NRLF and kenaf, some fundamental concept of filler materials and reinforcement, the technology to developments NRLF, and NRLF composites.
3. **Chapter 3:** Chapter 3 contains the information of the materials and equipment used in this research, the research flowchart and the experimental procedures adapted in this research.

4. **Chapter 4:** Chapter 4 consist of 5 series of study about kenaf filled NRLF. The first series was about the effects of kenaf loading on various properties of kenaf filled NRLF. The second series covered on the effects of partial replacement of kenaf powder by corn starch as a co-filler on the various properties of kenaf filled NRLF. The third series was about the effects of corn starch as a co-filler on properties of kenaf filled NRLF. The fourth series was about the effects of treated kenaf by alkaline treatment on kenaf filled NRFL and the last series was about the effects of prevulcanization of NRL on properties of kenaf filled NRL.
5. **Chapter 5:** Chapter 5 concludes the findings of this research work. The assessment on fulfilling the objectives and recommendations for future directions of this study were also include.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction to the natural rubber latex

Havea brasiliensis or rubber tree is a type of tropical plant originated from the Amazon, Brazil (Corpuz, 2013) and extensively cultivated in Southeast Asia such as in Malaysia, Indonesia, Philippine, Myanmar, Vietnam, Cambodia, and Thailand (Claramonte et al., 2010) mostly due to its ability to produce NR, which is the most popular product of rubber plantations (Kush et al., 1990; Mokhatar et al., 2011). Malaysia has approximately 1 021 540 hectares of rubber plantations reported in 2009 that is capable of producing more than 120 000 tons of rubber seed annually (Gimbun et al., 2013).

Rubber tree can grow up to 20-30 meters in plantation (Corpuz, 2013). The wood from rubber trees can be used to make furniture (Mokhatar et al., 2011). Rubber trees reproduce by bursting of the ripened fruits, scattering the seed to the surrounding area. As mentioned before in chapter one, NR is obtained from the Havea Brasiliensis or rubber trees. Latex is the cytoplasm of latifiers or specialized cells in the rubber tree. It also known as a naturally occurred, anionically stable colloidal dispersion of polyisoprene polymer dispersed in an aqueous medium. In other words, natural rubber latex is naturally originated, anionic type polyisoprene rubber dispersion in an aqueous medium. Lactifiers are damaged during tapping or removing of the bark, causing the latex to flow out.

When the latex is exposed to air, it will coagulate and can be processed into NR. Coagulation of the latex is the aggregation of rubber particles, which is a defense mechanism in rubber trees against pathogens (Gidrol et al., 1994). The composition of the NR latex in Table 2.1 was varying from source to source as it influences by various factors such as soil conditions, season, clone, fertilizer application techniques and tapping frequencies (Liyanage, 1999).

Table 2.1: Typical composition of NR latex (Kalyani, 1999).

Composition	**% by weight of latex**
Dry rubber content	30 – 35
Proteinous substances	1 – 1.5
Lipids	1 – 2.5
Sugars	1
Inorganic Ions	1
Water	60 - 65

The chemical structure of rubber content in the NR latex is identified as linear cis-1,4-polyisoprene as shown in Figure 2.1 (Matador rubber, 2007). Polyisoprene is a polymer having a broad molecular weight distribution with a high structural regularity. Due to this reason, NR tends to crystallize spontaneously at low temperatures or when it is stretched. NR exhibit outstanding tear and tensile strength, resilience and flexibility due to its high molecular weight and chemical nature (Wijesinghe et. al., 2016).

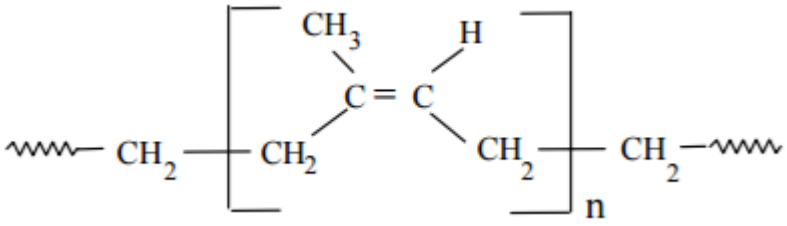


Figure 2.1: Chemical structure of cis-1,4-polyisoprene (Matador rubber, 2007).

Rubber suspension in latex are polyisoprene that can vary from 20-60% of the total wet weight of latex (Martin, 1991), which needs to be coagulated to obtain the rubber. NR is involved in industries such as biomedical, tire, shoes, mattress and adhesives (Okomo et at., 2011). NR latex has several properties that make it useful such as elastisity, high mechanical strength, impermeable to liquid, high flexibility, low heat buildup, and resilience (Mantello et al., 2012; Riyajan and Sukhlaaied, 2013). On the other hand, the downsides of NR cannot be ignored, such as sensitive to chemical and solvents, low flames resistance, and difficult to degrade (Riyajan and Sukhlaaied, 2013).

2.2 Foam manufacturing

2.2.1 Synthetic foam manufacturing

Production of polyurethane foam has a higher demand in foam manufacturing. The basic steps in production of flexible polyurethane foam are involving the condition of raw material, mixing, growth, cell opening and cure (Housel, 2004). The raw material need to be consistent as it is important in the fate of foaming mass. Gas molecules from air are dissolved in polyol and isocyanate during transportation and storage. It is important

for cell nucleation in mix head. The insufficient dissolution of raw material, causes the cell structures of the foam become more course. Mixing process occured in mix head as the isocyanate is mixed with water, polyol and other ingredient. Mix head functions as a mixer for the ingredients and formation of the bubble nuclei in the foam.

The formation of cell nuclei can be occurred when the air cavities are dissolved into tiny bubble seeds. The cell started to expand as the blowing gas like volatile additives, chlorofluorohydrocarbons (CFC) or hydrofluorocarbon (HFC) trapped inside the closed cell and produce carbon dioxide as the blowing gas after reacted with water and isocyanate. Then, the cell opening is formed and needed in order to have good properties of foam. The gas pressure is vented to the atmosphere for curing process. Polyurethane foam used either slabstock machine or moulding machine (Sivertson, 2007).

2.2.2 Latex Foam Manufacturing

Two types of latex foam manufacturing methods can be identified in literature. One method is called ―Dunlop method and the other is known as Talalay process. Talalay process is not a popular method in industries due to the high amount of capital investment and the complicated manufacturing techniques. Dunlop process is mostly used in industries due to its simple method of production and the low capital cost requirement of making a production line. Dunlop method can be divided into two major categories based on the foaming techniques known as batch process and continuous process. In the batch process, the foaming of the liquid compounded latex is done by an industrial type beater famously known as Horbart mixer. In the continuous manufacturing process,

foaming of liquid compounded latex is done by continuous foaming machines. Today several brands of foaming machines can be seen in industries. Among them Oakes foaming machine is the most famous and a good quality foaming machine fabricated by the USA family company called Oaks (http://www.oakes.com).

The liquid foam is gelled using gellation by adding gelling agent and poured into required shaped mould. The mould can have many shapes and sizes depending on the end product of the latex foam product. The typical mould used for manufacturing mattresses in industries has aluminium pins made from alloy materials (Alloy and Temper: 1100-H14, Thickness Tolerance: 20 µm, Ultimate Strength: 15500 psi). The side walls of the mould would probably be the same material or stainless steel, but the stainless steel moulds are not the common type in industries due to the huge weight and unmanageable heat build-up. The sizes and the shapes of the moulds absolutely depend on the required sizes and the shapes of the final product of latex foam. The production of thicker products such as mattresses is carried out in very large moulds. A huge amount of aluminum pins is used to facilitate heat transferring inside the thick natural rubber foam products. The shapes, sizes and the distribution pattern of the pins mostly depend on the customer requirements. The Figure 2.2 shows the cross section of the moulds that have different top and bottom pin alignments. Mould design and mould construction for the manufacturing of products in natural rubber foam industries is a very important process (Blackley, 1966a).

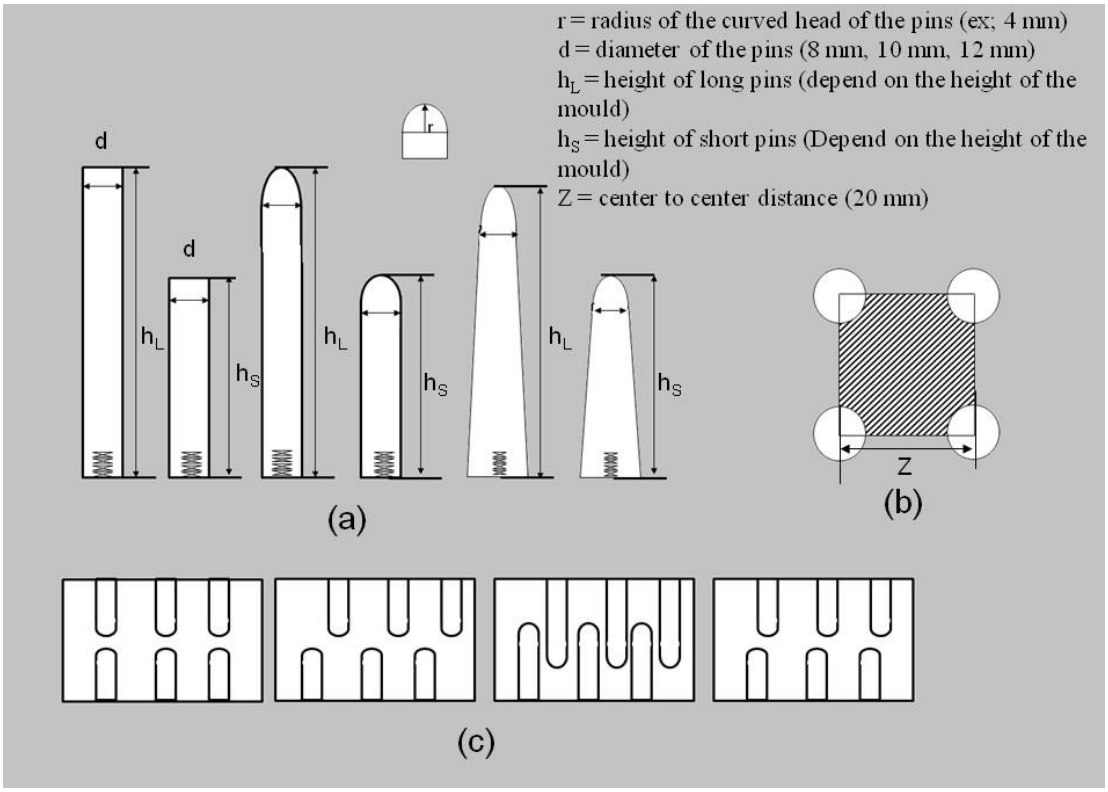


Figure 2.2: Mould design and mould construction in latex foam production

(Blackley, 1966a; Madge, 1962)

The first step of the manufacturing process starts with grinding of powdered raw materials into dispersion forms using water as the media (Blackley, 1966a; Joseph, 2013).. Then the dispersions are stored in storage tanks which are equipped with mechanical agitators that rotate 24 hrs to prevent from possible sedimentation of the dispersions. Next these dispersions are mixed with raw latex according to the formulation and stored in compounding tanks. Raw latex storage tanks also consisted with mechanical stirrers that rotate all the time to prevent separation of water from rubber in the latex. Then the compounded latex in the compounding tanks are matured up to 8-12 hrs and then transferred to the production plant and stored in the compounded batch tank.

2.3 Development of NRLF

The fact that the latex foam industry saw the beginning of its true development in the late 1920's was no accident but many ways a fulfillment. In 1914, an attempt was made tom produced sponge rubber latex. Schidrowitz and Goldsbrough reported in a British patent (BP) called Improving rubber substance in making a porous or spongy rubber product using rubber latex and ammonium carbonate as the blowing agent (Schidrowitz and Goldsbrough, 1914). In 1929, patents from Dunlop Rubber Company mentioned that a foam could be solidified into stable structure by a variety of methods, the solidified foam structure being subsequently dried and vulcanized. The idea had now taken shape that it was possible to produce a composites dispersion of air and rubber globules which could be so treated that a controlled coalescence and coagulation of disperse rubber phase could carried out without a simultaneous air coalescence, or at least only a partial coalescence of the disperse air phase. This simple phenomenon is the one that makes the production of latex foam rubber possible (Madge, 1962).

2.4 General principles of NRLF

NRLF products are cellular (open cell, close cell or a combination of open and close cell structure) directly produced from liquid latex compounds. The skin is smooth surface formed by contact with mould surface. There are three basic steps in the latex-foam product manufacture which is foaming of compounded latex by introduction of air (or other gases), gelling of foamed latex in the suitable mould and follow by vulcanization of foam.

Foam latex compound is a three-phase colloid system (two disperse phases- rubber and air and third continuous phase of modified latex). Two principle interfaces are serum-rubber and serum-air. Successful manufacture of latex foam depends on the manipulation of these interfaces. The gelation of foam destabilizes the serum-rubber interface so that rubber particles come together to form a uniform structure which make the foam structure rigid.

The condition which help destabilization of serum-rubber interface also lead destabilization of serum-air interface. If the serum-air interface destabilizes first, the foam will collapse. Hence, the gelling of serum-rubber interface must occur first to form rigid foam which resist collapse due to destabilization of serum-air interface. The sequences are controlled by type of gelling agent, time and temperature adjustment in the process. If the limited collapse is intentionally allowed, a closed cell structure will result.

2.5 Natural rubber latex foam based on Dunlop method

2.5.1 Preparation of dispersion

Preparation of dispersion is a very important step in making a good quality natural rubber latex foam product. According to the theory of mixing chemicals to the latex dispersion, the size of the raw materials and the alkalinity of the raw materials should match with that of natural rubber latex dispersion (Blackley, 1966c). To match the particle sizes of raw materials with the particle size of natural rubber latex foam, the grinding of dispersions is a very important step. The grinding time of the dispersion totally depends on the required average sizes of the particles in dispersions. Total solid content of

dispersions is measured according to the ISO 124:1992 (E) methods in the lab. The pH values are determined by the commercial pH meters. To make good quality dispersion, addition of a small amount of dispersion agent is required. There are lots of surface active agents such as sulphonates (Sodium poly [(naphthaleneformaldehyde) sulfonate] commercially known as TAMOL), anionic organic Sulphates (Sodium dodecyl/lauryl sulphate commercially known as TAXAPON), cationic (Lauryl pyridiniun chloride), and amphoteric (c-celyl betaine). Non-ionic Condensation products of ethylene oxide with fatty acids, fatty alcohols or phenols (Synopol PEG 400, Polyethylene glycol) are used as dispersion agents in various industries. Among them TAMOL is a famous dispersion agent in the preparation of stable dispersion in natural rubber latex foam industries. A small amount of Bentonite clay is also mixed with the dispersions to increase the colloidal stability of the dispersions. Grinding of the raw materials to make colloidal dispersions in aqueous medium should be carried out by means of milling process. This process consists of four different steps such as wetting of particle surfaces, separation of agglomerates and aggregates into individual particles, attrition or fracture of individual particles into smaller particles and adsorption of dispersant by particle surface to obtain a stable dispersion (Morrison, 2001). In foam rubber manufacturing industries the above explained steps are done by an industrial type ball and Jar mills or vertical or horizontal type. Preparation of dispersions in the lab can be carried out by a small lab scale ball mill. In industries, the operation of making dispersion can be either batch process or the continuous process (Blackley, 1966c; Joseph, 2013).

In the preparation process of dispersions, the total solid contents (TSC) are always kept as higher than the required TSC for the compounding step. After preparation the

dispersions, required TSC is obtained by adding sufficient amount of water to the dispersion storage tank. Nevertheless, in the preparation of sodium silicofluoride (SSF) dispersion, the TSC adjustment is done at the last moment, i.e. just before the addition of SSF to the compound. This is very important to prevent unnecessary hydrolysis of SSF in the presence of water. In addition, the time of SSF dispersion storing should be kept as low as possible to have a good quality SSF dispersion. Because of this reason, in industries, preparation of SSF dispersion is done almost every day.

2.5.2 Compounding process

The next major step in the process of making foam rubber is compounding where all the required materials are mixed together in a container equipped with a low speed stir according to the formulations. In the industries the compounding tank is probably a jacketed type tank, made out from stainless steel; the outer jacket is used to control the temperature by circulating chilled water (Madge, 1962). Table 2.2 shows the typical industrial scale formulation of the compounding batch for the preparation of NRLF by the Dunlop method.

Table 2.2: Typical formulation of latex compound in the synthesis of latex foam rubber samples by the Dunlop process using natural rubber latex as the main raw material (Madge, 1962).

Ingredients	**Dry parts per hundred rubber (phr)**
60 % NR Latex	100.00
20 % Potassium oleate Soap	2.00
50 % Sulphur	2.5
50 % Phenolic type Antioxidant	1.00
50 % ZMBT	1.00
50 % ZDEC	1.00
40 % ZnO	3.00[a]
40 % DPG	0.30-0.50
30 % SSF	1.00[b]

a- can be varied from 1-5 phr depending on the gelling time of the compounded latex
b- can be varied from 1.00 – 4.00 phr depending on the gelling time of the compounded latex

2.5.3 Foaming and gelation technique

In Dunlop method, compounding mixer is consisted of potassium oleate soap or any other suitable long chain carboxylate soap such as ammonium oleate soap, castore oil soap etc. which acts as the foam promoter. Once the compounding mixer is beaten mechanically by means of rotating wire whisks or a rotating mixing head, the compound will get air bubbles inside it. In Industries, there are two major techniques used to introduce air bubbles into the prepared latex compound, one is called batch foaming technique where the foaming of the compounded latex is accomplished by a wire whisks

rotating in planetary movement. The other technique is called continuous foaming technique where the foaming of compounded latex is done by a mixing head equipped with a pneumatic airline which can control the amount of frothing or is rather called the density of the final product (Madge, 1962). In the old days, the foam rubber industries also used the batch foaming technique, but nowadays most of the industries use the continuous foaming technique using more and more sophisticated continues foaming machines. Preparation of natural rubber latex foam in a lab by the batch foaming technique can be carried out by using planetary mixers (Figure 2.3)

Figure 2.3: 5 litters planetary mixer (www.hobartcorp.com; www.kenwoodworld.com)

Once the foaming step is completed, the next important step is the gelling step. A large number of tiny air bubbles inside the foamed liquid latex compounding dispersion has to be stable and should make stable solid-air system by gelling the rubber part of the liquid latex dispersion. The gelling time of the compounds depends on many factors such

as the alkalinity of the compounded latex, temperature of the compounded latex, composition of the foam promoters (Madge, 1962).

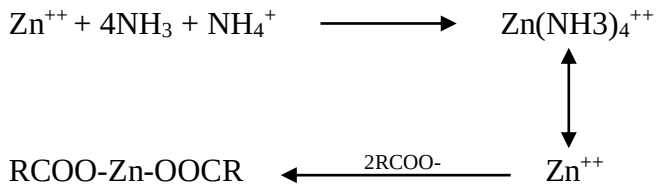
There are two major types of gelling systems can be explained in the production of latex foam. One is called heat gelling system, where the compounded latex having heat sensitizing gelling agent is gelled by applying heat. The other system called Delayed-action gelling system is the gelling of the rubber phase happening due to the dropping of pH with the time by fluoro chemicals. The most common type fluoro chemicals are fluosilicates, fluostannates, fluotitanates etc. In the Dunlop method, the gelling of the foamed compounded rubber is carried out by the combination of sodium silicofluoride and zinc oxide. In the final part of the foaming process, 3 phr of 40 % primary gelling agent (ZnO) together with 0.30 phr of 40 % curing activator (1,3-Diphenylguanidine) is mixed thoroughly with the foamed compounded latex and finally 1-1.5 phr of 25 %-30 % secondary gelling agent (SSF) is immediately added to it and is poured into the required shape mould. The hydrolysis of SSF can be shown as following reactions. Reaction 2.1 shows the first disintegrating of di-sodium silicofluoride into sodium and hexa-fluorosilicate ions whereas the reaction 2.2 shows the hydrolysis of hexa-fluorosilicate into several ions by water (Madge, 1962; Calvert et al., 1982).

$$Na_2SiF_6 \longleftrightarrow 2Na^+ + SiF_6 \qquad 2.1$$

$$SiF_6 + 4H_2O \longleftrightarrow Si(OH)_4 + CH_4 + 6F^- \qquad 2.2$$

Moreover, there can be explained three steps of reactions in the SSF gelation in the presence of ZnO. Hydrofluoric acid reduce the pH of the latex froth, Silicic acid has the adsorptive effect on the froth and the zinc amine complex formed due to the reactions

of ZnO with ammonia presence in the latex foam compound which can destabilize the froth. In the presence of ammonia the Zn++ from ZnO can form a complex containing anions of fatty acid soap (potassium oleate soap). This zinc ammine system is a heat sensitive gelation system, when the temperature of the froth is increased this system can also be stimulated and speed up the gelling of the latex. So it is advisable to keep the temperature of the foamed latex compound in an ambient temperature or lower than ambient temperature to prevent rapid gelation. At the same time, the mould temperature should be maintained at the ambient temperature or slightly higher than the ambient temperature (35 °C – 50 °C). If the froth gelled too quickly, it is very difficult to pour the liquid stage foam into the mould and also the defects due to rapid gelling can be seen in the end product. The zinc ammine heat sensitive gelation system can be explained as follows. The reaction 2.3 shows the steps of zinc amine gellation system (Calvert et al., 1982).



2.3

(Anion from fatty acid soap)

Depending on the parameters of the compound such as the alkalinity of the compound, the parameters of the latex that is used for the compound preparation, temperature of the compounded latex, the actual amount of the gelling agents will be varied. In the industries, the gelling time that is the time taken to solidify the liquid dispersion of frothed rubber compound is kept in between 3-5 minutes. Within this time